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(71) Applicant  
**Castrol Limited**  
  
(Incorporated in the United Kingdom)  
  
**Burmah Castrol House, Pipers Way, Swindon,  
Wiltshire, United Kingdom**

(72) Inventors  
**Christopher William Livesey  
Andrew Jonathon Markson**

(74) Agent and/or Address for Service  
**John Anthony Claisse  
97 Portway, Wells, Somerset, BA5 2BR,  
United Kingdom**

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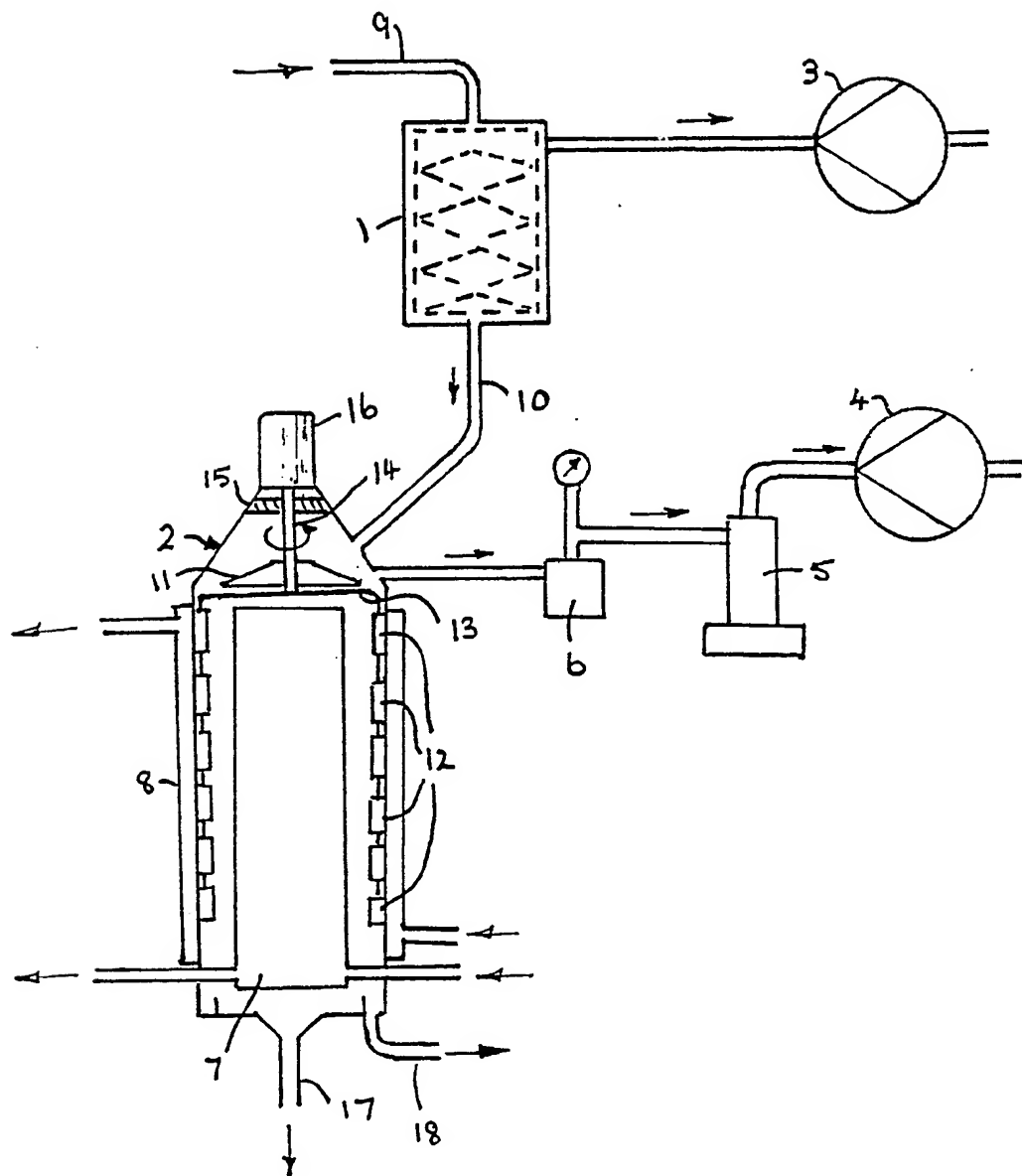
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(54) **Purification of diethanolamides**

(57) A method of removing diethanolamine from a diethanolamide containing diethanolamine involving subjecting the diethanolamide containing the diethanolamine to molecular distillation to distil off the diethanolamine. The present invention reduces the risk of the diethanolamide undergoing reaction during the distillation and it is of particular value for diethanolamides derived from long chain carboxylic acids.

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### PURIFICATION PROCESS

This invention concerns the purification of diethanolamides.

Diethanolamides are widely used as foam boosters, foam stabilizers, viscosity controllers, surfactants, emulsifiers and corrosion inhibitors in the detergent, cosmetic, textile and metal working industries. Typically, diethanolamides are prepared by reacting diethanolamine with a carboxylic acid, usually an aliphatic carboxylic acid, the molar ratio of amine to acid generally being about 2:1. As an alternative, diethanolamine is reacted with the methyl ester of the carboxylic acid, but in a molar ratio of about 1:1, to form a so-called "super amide". A wide range of carboxylic acids, or their esters, is used to prepare such diethanolamides.

As a result of the large number of functional groups in both the reactants and the products of these reactions, the desired products contain many different impurities and in different amounts depending upon the reaction conditions. Typical by-products include amide mono- and di-esters in which the hydroxyl groups of the desired product have reacted with free carboxylic acid or its methyl ester, amido amines in which hydroxyl groups of the desired product have reacted with free diethanolamine, and 1,4-diethanol piperazine formed

by condensation and cyclisation of diethanolamine. In addition, unreacted diethanolamine is generally present, often in amounts of as much as 20-30% by weight of the reaction product depending on the method of preparation of the amide.

Although the presence of unreacted diethanolamine in these products may not seriously affect the ability of the products to function in a particular way, diethanolamine is considered to be a hazardous material, and it is desirable to reduce the free diethanolamine content of the products, for example to 1% or less.

Altering the reaction conditions used to produce the diethanolamides in an attempt to reduce the amount of unreacted diethanolamine in the product is generally unsatisfactory as it usually leads to increased amounts of by-products which adversely affect the properties of the diethanolamides for the intended end use. Attempts to remove unreacted diethanolamine by distillation even under reduced pressure using a rotary evaporator or a rotary vacuum pump are also generally unacceptable since heating the impure diethanolamide to effect the distillation causes further chemical reactions to take place, for example by inter- and intra-molecular reactions of the desired diethanolamide and/or by products. The result can be a product with a lower diethanolamine content, but at the expense of generating by-products which make the product less desirable or even useless for the intended end use.

According to the present invention there is provided a method of removing diethanolamine from a diethanolamide present therein, the method comprising subjecting the contaminated diethanolamide containing the diethanolamine to molecular distillation to distil off the diethanolamine.

By molecular distillation is meant a vacuum distillation

process in which a liquid is evaporated under a low pressure from an evaporating surface and condensed on a condensing surface which is spaced from the evaporating surface by a distance which is smaller than or comparable with the mean free path of the molecules in the vapour at the pressure employed. Said distance is usually between 5 and 50 mm and said pressure is typically between  $10^{-2}$  and  $10^{-4}$  Torr. The molecular distillation technique is known per se.

The present invention enables a surprisingly rapid and efficient removal of diethanolamine from diethanolamides to be achieved. It is furthermore possible to achieve this under mild conditions so that the diethanolamides undergo little or no reaction during the removal.

Any of a variety of diethanolamides can be subjected to purification using a method in accordance with the invention. Examples of acids from which they can be derived include long chain aliphatic carboxylic acids, and especially such acids containing from 10 to 22 carbon atoms.

In a preferred embodiment of the present invention, the evaporator of the molecular still is heated to a temperature of about 100°C. The preferred pressure, as measured over a cold trap of the still, is between  $10^{-2}$  and  $10^{-4}$  Torr. Preferably, the evaporator surface of the molecular distillation apparatus is wiped during the distillation process. Preferably, the contaminated diethanolamide is initially fed through a degassifier.

An embodiment of the invention will now be described, by way of example, with reference to the accompanying diagrammatic drawing which is a diagrammatic elevation of the embodiment, partially in section, of apparatus for removing diethanolamine from diethanolamides.

The illustrated apparatus includes a degassifier 1, the

outlet of which being connected to a molecular still 2. The degassifier 1 is exhausted by a rotary vacuum pump 3. The molecular still 2 is exhausted via a vacuum line consisting of a rotary vacuum pump 4, a diffusion pump 5, and an intermediate cold trap 6. The pressure above the cold trap is maintained at between  $10^{-2}$  and  $10^{-4}$  Torr.

The molecular still 2 is provided with a tubular water-cooled condenser 7 and an exterior heated oil jacket 8, the oil in the jacket 7 being maintained at about 100°C.

In use, a diethanolamide containing for example 20-30% of diethanolamine is fed continuously, and at a controlled rate, into the degassifier 1 through the conduit 9. Dissolved air and any other gasses present are exhausted through the pump 3. The degassified diethanolamide then flows from the degassifier via conduit 10 into the molecular still 3 on to a distributor 11 so as to form a thin film on the cylindrical heated outer wall of the still 2. This wall forms the evaporator surface of the still, this surface being continuously wiped by polytetrafluoroethylene rollers 12 which are suspended from a cage 13. Cage 13 is continuously rotated by a drive shaft 14 which runs through a vacuum seal 15 and is driven by a motor 16 at a speed of approximately 120 r.p.m.. This is sufficiently fast to hold the rollers 12 against the film of impure diethanolamide by centrifugal force so that the rollers 12 continuously renew the film surface by a rolling action.

Diethanolamine is rapidly evaporated to the tubular condenser 7 which is spaced by a few millimetres from the inner surface of the heated outer wall. Small quantities of diethanolamine which are not condensed are removed by the cold trap 6. After a single pass, purified diethanolamide fed from the still 2 via conduit 17 will usually have a diethanolamine content of about 1% or less if the diethanolamide fed to the apparatus has a diethanolamine content of about 20-30%.

Diethanolamine removed in the distillation leaves the still 2 via conduit 18. The short residence time of the diethanolamide at the elevated temperature within the still 2 furthermore results in little if any production of further by-products, and it has been found to be acceptable for use as a surfactant, for example for metal working fluids.

As will be appreciated by those skilled in the art, particularly low levels of residual diethanolamine can be achieved by the use of multi-stage molecular stills in which the diethanolamide from one still is fed to the input of another still. This may, if desired, be effected using two or more individual stages of molecular distillation.

Particularly preferred molecular stills for use in effecting the present invention are supplied by UIC GmbH, Alzenau, Germany.

Claims

1. A method of removing diethanolamine from a diethanolamide having diethanolamine therein, the method comprising subjecting the diethanolamide containing diethanolamine to molecular distillation to distil off diethanolamine.
2. A method according to claim 1, wherein the diethanolamide is subjected to molecular distillation in a first molecular still, and then again in a second molecular still.
3. A method according to claim 1 or claim 2, wherein the diethanolamide is formed into a heated liquid film which film is wiped during said molecular distillation.
4. A method according to claim 3, wherein the said film is wiped by a rolling action.
5. A method according to any of the preceding claims, wherein the diethanolamide containing diethanolamine is passed through a degassifier before being fed to the still.
6. A method according to any of the preceding claims, wherein the pressure in the still, as measured over a cold trap connected thereto, is between  $10^{-2}$  and  $10^{-4}$  Torr.
7. A method according to any of the preceding claims, wherein the impure diethanolamide is passed to the still at a controlled rate.
8. A method according to any of the preceding claims, wherein the diethanolamide has been prepared by reacting diethanolamine with a carboxylic acid in a molar ratio of approximately 2:1.
9. A method according to any of claims 1 to 7, wherein the



diethanolamide is a "super amide".

10. A method for removing diethanolamine from a diethanol-  
amide, the method being substantially as herein described  
with reference to the accompanying drawing.

11. Diethanolamide when subjected to a method according to  
any of the preceding claims.

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